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Applicant	
Identification Number	: 391008456
Name	: MASUMOTO Takeshi
Address	: 8-22, Kamisugi 3-chome, Aoba-ku, Sendai-shi, Miyagi, Japan
Applicant	
Identification Number	: 591112625
Name	: INOUE Akihisa
Address	: Kawauchi-Jutaku 11-806, Motohasekura 35, Kawauchi, Aoba-ku, Sendai-shi, Miyagi, Japan
Applicant	
Identification Number	: 390025922
Name	: Tomy International
Address	: 11-2, Tamagawa 4-chome, Chofu-shi, Tokyo, Japan

Inventor

Name : MASUMOTO Takeshi

Address : 8-22, Kamisugi 3-chome, Aoba-ku, Sendai-shi, Miyagi, Japan

Inventor

Name : INOUE Akihisa

Address : Kawauchi-Jutaku 11-806, Motohasekura 35, Kawauchi, Aoba-ku, Sendai-shi, Miyagi, Japan

Inventor

Name : CHIYOU Tou

Address : Room No. 104 of Hirose New Life, 10-12, Tsuchitoi 1-chome, Aoba-ku, Sendai-shi, Miyagi, Japan

Inventor

Name : MOCHITATE Mikio

Address : 417-2, Aza-Kanayadaira, Oaza-Shimonogami, Okuma-machi, Futaba-gun, Fukushima, Japan

Inventor

Name : NISHI Kikuo

Address : 1-121, Hashimoto-cho, Haramachi-shi, Fukushima, Japan

Attorney : ICHIHASHI Shunichiro, Patent Attorney

[TITLE OF THE INVENTION]

METAL DENTURE BASE FOR DENTAL APPLICATIONS

[ABSTRACT]

[OBJECT] In is an object of the present invention to provide a metal denture base for dental applications, which is inexpensive, excellent in adaptability, and high in intensity.

[CONSTITUTION] A metal denture base having the foregoing advantages can be obtained by forming a metal denture base for dental applications from an amorphous alloy having a supercooled liquid region, because a heating up to a predetermined temperature and a highly-accurate superplastic forming can be performed.

[CLAIMS]

[Claim 1] A metal denture base for dental applications, comprising an amorphous alloy having a supercooled liquid region.

[Claim 2] The metal denture base for dental applications according to Claim 1, wherein the supercooled liquid region is 20K or more.

[Claim 3] The metal denture base for dental applications according to Claim 1 or 2, wherein an amorphous alloy is contained at a ratio of 30% or more.

[Claim 4] The metal denture base for dental applications according to any one of Claims 1 to 3, which comprises an amorphous alloy having the following composition:

General Formula: Xa-Yb-Mc

where

X represents one or more metals selected from the group consisting of Zr, Ti, Hf, Mg, and rare earth metals;

Y represents one or more metals selected from the group consisting of Al, Zr, Hf, Ti, and rare earth metals;

M represents one or more metals selected from the group consisting of transition metals such as Fe, Co, Ni, and Cu; and

a = 30 to 80, b = 5 to 20, and c = 0 to 60.

[Claim 5] The metal denture base for dental applications according to Claim 4, which comprises an amorphous alloy having a composition selected from the group consisting of:

Zr_{63}-Al_{12}-Co_{3}-Ni_{7}-Cu_{15};

Zr_{60}-Al_{15}-Co_{5}-Ni_{15}-Cu_{5};

Zr_{65}-$Al_{7.5}$-$Cu_{27.5}$;

Zr_{55}-Al_{20}-Co_{20};

Zr_{70}-Al_{15}-Fe_{15}; and

Zr_{60}-Al_{15}-Ni_{25}.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION]

The present invention relates to an improvement in metal denture bases for dental applications, which can be widely used not only for ordinary partial dentures and complete dentures but also for bridge dentures.

[0002]

[PRIOR ART AND PROBLEMS THEREOF]

As a denture base used for a partial denture or a complete denture, a denture base made of acrylic resin has been frequently used, because it can be readily manufactured and adjusted in accordance with a palate or an alveolar ridge of a patient. However, since the denture base made of acrylic resin easily fractures and has a considerable thickness, a patient may have an unpleasant feeling. In addition, there arises a problem that taste of food may be changed by unpolymerized monomers. Further, the denture base made of acrylic resin incurs a volume reduction of approximately 10%, thus forcedly requiring subsequent adjustments by a dentist about ten times. Therefore, the denture base made of acrylic resin is not clinically satisfactory.

[0003]

For redressing these disadvantages, there have been proposed a denture base made of polysulfone resin and a denture base made of cobalt-chrome alloy, gold alloy, and palladium alloy. The former denture base made of polysulfone resin certainly has improved intensity as compared with the conventional ones made of acrylic resin, but nevertheless it basically fails to completely solve the problems involved in denture bases made of resin. The latter denture base made of metal can secure intensity and thinness, but it is manufactured by a so-called investment casting method and therefore requires complicated steps and procedure. Thus, a denture base in itself becomes high in cost, and, in addition, involves a serious problem that a dimensional accuracy disorders due to its contraction caused in cooling and solidification of a heated molten metal.

[0004]

In recent years, the above-mentioned cobalt-chrome alloy and the like are replaced with titanium or titanium alloy, because the titanium or titanium alloy has no virulence, does no harm to living bodies, and is chemically stable. However, the titanium is a very active metal under a high temperature, and easily coupled with oxygen and nitrogen, to considerably spoil original properties of titanium. Therefore, in its casting method, differently from the denture base made of cobalt-chrome alloy, etc., an investment and a crucible has to be made of a special material of magnesia, calcia, or zirconia system that never react with titanium. In addition, since the casting has to be performed under vacuum or argon gas substituted atmosphere, a large-sized device of high cost is required. Further, since a contraction caused when a molten metal heated to 1700 degrees C is cooled and solidified is still unignorable, the denture base often fails to fit to a palate or an alveolar ridge of a patient.

[0005]

Thus, a denture base formed by titanium-pressing, in place of the denture base formed by such a complicated and expensive titanium-casting, is now attracting attention. This titanium pressing method utilizes a superplastic phenomenon of Ti-6Al-4VELI alloy. In this method, used is a flat plate of titanium alloy having a thickness of 0.5 mm and an initial crystal grain size of approximately 4 μ, and a model of jaw is formed from a fireproof and rigid molding material for exclusive use. Then, a press-working is performed for half an hour to one hour under a high-temperature argon gas atmosphere of 850 degrees C, to thereby manufacture a denture base.

[0006]

[PROBLEMS TO BE SOLVED BY THE INVENTION]

In this method, however, a fireproof and pressure-proof molding material having high intensity is required for its exclusive use, and the press-working has to be performed under an inert gas atmosphere in order to avoid deterioration in reaction at high temperatures. In addition, a material must be so adjusted as to have a crystal grain size suitable for a superplastic forming, and there is a serious problem of ill adaptability to a patient. Further, when artificial teeth are arranged on the denture base obtained by the titanium-pressing and fixed thereto by means of resin-polymerization, a contraction of the resin may cause a deformation of the denture base.

[0007]

[MEANS TO SOLVE THE PROBLEMS]

In view of the above, it is an object of the present invention to provide a metal denture base for dental applications, comprising an amorphous alloy having a supercooled liquid region. A metal denture base of the present invention adopts an amorphous alloy doing no harm to living bodies and having a supercooled liquid region that is chemically stable even within a mouth. Therefore, a heating up to a predetermined temperature and a highly-accurate superplastic forming can be performed through a simpler process than the conventional titanium-pressing process. As a result, there can be obtained for the first time a metal denture base which is inexpensive, excellent in adaptability, and high in intensity.

[0008]

In particular, when an amorphous alloy having as wide a supercooled liquid region as 20 K or more is adopted or when an amorphous alloy is contained at a ratio of 30% or more, a superplastic phenomenon can be obtained with a relatively small force within a predetermined temperature range, which is incommensurable with a superplasticity of the aforementioned Ti-6Al-4VELI alloy. More specifically, the Ti-6Al-4VELI alloy exhibits a superplasticity of 1000% at 850 degrees C, while the

present invention exhibits a superplasticity of approximately 800% at 443 K (170 degrees C) and approximately 15000% at 473 K (200 degrees C) without causing any fracture.

[0009]

As a specific example, there can be mentioned an amorphous alloy having the following composition: General Formula: Xa-Yb-Mc, where X represents one or more metals selected from the group consisting of Zr, Ti, Hf, Mg, and rare earth metals; Y represents one or more metals selected from the group consisting of Al, Zr, Hf, Ti, and rare earth metals; M represents one or more metals selected from the group consisting of transition metals such as Fe, Co, Ni, and Cu; and a = 30 to 80, b = 5 to 20, and c = 0 to 60. Thus, since Zr, Ti, and Hf, etc., which serve as fundamental elements, hardly do harm or virulence to living bodies, they are best suited for a metal denture base that is always worn within a mouth. The M elements Fe, Co, Ni, and Cu coexist with the elements Zr, Ti, and Hf and improve an amorphous formability.

[0010]

Further preferable representative examples among these include (1) Zr_{63}-Al_{12}-Co_3-Ni_7-Cu_{15}; (2) Zr_{60}-Al_{15}-Co_5-Ni_{15}-Cu_5; (3) Zr_{65}-$Al_{7.5}$-$Cu_{27.5}$; (4) Zr_{55}-Al_{20}-Co_{20}; (5) Zr_{70}-Al_{15}-Fe_{15}; and (6) Zr_{60}-Al_{15}-Ni_{25}.

[0011]

[EXAMPLES]

The present invention will hereinafter be described through specific examples. First, as shown in FIG. 1, a mother alloy 1 having each of the aforementioned (1) to (6) compositions was put in a quartz nozzle 2. The quartz nozzle 2 was formed, at its tip end, with a small hole 2a having a diameter of 1.0 to 2.0 mm. The quartz nozzle 2 was then subjected to an induction heating under a vacuum pressure, for dissolution of the mother alloy. Then, the quartz nozzle 2 was moved down and applied with a pressure of argon gas, so that a molten metal was spouted from the small hole 2a out into a copper die 3 and rapidly cooled down at a cooling rate of 10^4 to 10^7 K/s, to thereby obtain a bulk material 4 having a size of 3.0 × 50 mm which served as a specimen. The mother alloy 1 was prepared by dissolving a sponge-like Zr metal within an arc furnace for degassing of the Zr metal and then put other elements into the furnace for dissolution thereof.

[0012]

In order to determine whether the bulk material 4 became an amorphous alloy, the bulk material 4 was subjected to a structure diffraction using an X-ray diffractometer. As a result, as shown in FIG. 2, an air-cooled bulk material 4 sharply exhibited a

presence of Zr, whereas a bulk material 4 having the alloy composition of (3) exhibited no clear peak within a region corresponding to a Kα-ray of Zr. It is preferabl that this amorphous alloy has an amorphous alloy ratio of 30% or more.

[0013]

Next, the amorphous alloys having the respective alloy compositions were subjected to differential scanning calorimetry (DSC curve) in order to examine their thermal properties. As a result, as shown in FIG. 3, the respective alloy compositions largely differed from each other in glass transition temperature Tg and crystallization temperature Tx. A maximum value of a supercooled liquid region ΔTx (Tx-Tg) was 56 K in case of (5) that included Fe, 69 K in case of (4) that included Co, 77 K in case of (6) that included Ni, and 88 K in case of (3) that included Cu. This revealed that the amorphous alloy having the alloy composition of (3) including Cu exhibited the widest supercooled liquid region ΔTx, which was determined by Tg and Tx existing in as low a temperature region as 630 to 710 K.

[0014]

FIG. 4 shows a constitutional ratio of the three elements and a composition-dependency of the supercooled liquid region ΔTx with respect to the amorphous alloy having the alloy composition of (3) including Cu, which was the best one of the above-mentioned DSC curves. As clearly seen from FIG. 4, it was 59 to 77Zr, 5 to 13Al, and 25 to 32Cu. In particular, the alloy composition of (3), i.e., Zr_{65}-$Al_{7.5}$-$Cu_{27.5}$, exhibited the widest supercooled liquid region ΔTx of 80 K. The alloy compositions of (1) and (2) exhibited 100 K and 90 K, respectively, though their illustrations are omitted herein.

[0015]

FIG. 5 shows stress-strain curves of the amorphous alloy having the alloy composition of (3) with respect to a temperature change around Tg immediately before the supercooled liquid region ΔTx. It can be seen that, at the point of *A* which exceeds Tg = 630K, strain is caused by very small stress. This indicates a superplastic phenomenon obtained in the supercooled liquid region ΔTx. In addition, revealed was that a deformation started with a relatively small stress even at 550 K and 590 K immediately before Tg, and thereafter the stress moderated so that the deformation progressed intermittently.

[0016]

The amorphous alloys having the alloy compositions of (1) and (2) that substitute Co, Ni, and Cu for $Cu_{27.5}$ were also subjected to the same differential scanning calorimetry (DSC curve) and examined for its relationship to a stress-strain curve and a

temperature, with substantially the same result obtained.

[0017]

Further, in a region of the room temperature and body temperature (37 degrees C), the amorphous alloys having the alloy compositions of (1) and (2) had a Vickers hardness of Hv 450 and a tensile strength of 1400 MPa, and the amorphous alloy having the alloy composition of (3) had a Vickers hardness of Hv 400 and a tensile strength of 1200 MPa. These are higher intensities than the currently used cobalt-chrome alloys and tetra-metallic alloys which have a Vickers hardness around Hv 300 and a tensile strength of 700 to 900 MPa, and than pure titanium and titanium alloys such as Ti-6Al-4VELI. Accordingly, even if a denture base is repeatedly attached and detached in a mouth of a patient over a long period, the denture base suffers from a little deformation or damage.

[0018]

Next, there will be described a specific example of a method for manufacturing a denture base using the amorphous alloy having the above-described properties. First, as shown in FIG. 6, a molten metal is spouted from a small hole 2a of a nozzle 2 into between a pair of copper rolls 5 that is rotating, to thereby obtain an amorphous alloy plate 6 (of approximately 10 cm) having a thickness of 0.5 mm. The thickness of the plate may be, though depending on purposes, 0.3 to 0.7 mm.

[0019]

A complete denture, which is used when no tooth is left, can be manufactured relatively easily. However, a partial denture, which is attached based on a footing of plural remaining teeth, has a complicated configuration as a matter of course and has to comprise a holding means such as clasps. Thus, a description of a method for manufacturing a denture base for partial dentures includes that for complete dentures, and therefore the method for manufacturing a denture base for partial dentures is described herein for convenience' sake.

[0020]

First, a dentist takes an impression of an entire jaw of a patient in accordance with a conventional method, and gypsum is poured into this impression, to prepare a working model. In case of forming a denture base through the titanium-pressing that is a prior art closest to the present invention, the gypsum must be very rigid and heat-resistant and moreover there is required a preliminary arrangement of, e.g., filling up an undercut in a gum portion under remaining teeth, etc. Unlike the titanium-pressed denture base, the amorphous alloy of the present invention requires neither special working model nor special processing on the model, because the

amorphous alloy of the present invention, as its characteristics, develops a superplastic phen menon far beyond common knowledge and this phenomenon arises within a range from about the glass transition temperature Tg to the crystallization temperature Tx (that is usually 300 to 400 degrees C).

[0021]

For example, a working model 10 (of upper jaw) of FIG. 7 having remaining teeth lacks fifth and sixth right teeth and sixth and seventh left teeth. A flame design is firstly performed on the working model 10 using a pencil. More specifically, a connecting portion 11, denture base portions 12, clasps 13, and retainers 14 are designed. Then, an outline groove 15, which serves as a measure of a trimming, is formed in the working model 10 using a scraper, etc. When there is an undercut in a gum portion under the remaining teeth, the undercut can arbitrarily be filled with working gypsum.

[0022]

Subsequently, as shown in FIG. 8A, the working model 10 is put into a heating furnace 21, and the aforementioned amorphous alloy plate 6 of 0.5 mm thickness is set thereon in a hermetic-sealing manner. Then, the heating furnace 21 has a top cover 22 put thereon, and is locked. A temperature in the heating furnace 21 is gradually increased. When the temperature reaches 300 degrees C, an exhaustion 23 is carried out at a lower part and a pressure application 24 is carried out at an upper part. In this case, differently from the conventional titanium-pressed denture base, an argon-gas pressure application under a non-oxidizing atmosphere is not required. The temperature in the heating furnace 21 is further increased and maintained at 350 degrees C. In this condition, the pressure application 24 and the exhaustion 23 are performed, so that the amorphous alloy plate 6 adheres onto the working model 10 in approximately five minutes, as shown in FIG. 8B.

[0023]

The working model 10, together with the amorphous alloy plate 6, is then cooled down and taken out. In this case, the amorphous alloy plate 6 sticks to the undercut portions under the remaining teeth, to result in difficulty of separation. Therefore, the working model 10 must be broken. However, this raises no problem because the working model 10 can be prepared in multiple, if necessary. In addition, the working model 10 can be removed more easily as compared with the conventional very rigid and heat-resistant model.

[0024]

Then, performed is a trimming along the above-described groove 15 formed on the working model 10. That is, the whole is roughly trimmed, and subsequently a

piercing of an alveolar ridge, on which artificial teeth are to be mounted, is performed, so that the clasps and the retainers are cut out. This rough trimming is performed using a fretsaw, etc., and the cutting out can satisfactorily performed using general tools for dental mechanics, such as a grinding stone or a cemented carbide cutter with a shaft. Besides, the amorphous alloy of the present invention has a tensile strength of 1200 to 1400 MPa at an ordinary temperature, as already stated. Accordingly, it is best suited particularly for a partial denture that requires a spring characteristics such as clasps or retainers, etc.

[0025]

Thus, afterward, the whole is polish-finished in accordance with a conventional method, and artificial teeth are mounted using a self-curing resin and the like. The resultant thing is attached within a mouth of a patient to examine its adaptability. This is because an incomplete adaptation causes inflammation or ulcer at a portion in strong contact therewith.

[0026]

In this case, the conventional titanium-pressed denture base requires a heat treatment up to approximately 900 degrees C for its reform for adaptation, to thereby cause an unignorable inaccuracy due to thermal contraction. In addition, when the self-curing resin for mounting the artificial teeth is curing, a stress arises, and this stress induces a deformation of the denture base. Therefore, such titanium-pressed denture base and cobalt-chrome-made denture base, etc., are difficult to reform in accordance with dry structures of a mouth or remaining teeth of a patient. Thus, a metal base layer of 0.3 mm thickness and a resin base layer of 0.3 mm thickness are laminated so that a portion of the resin in contact with the dry structure may be cut off or reinforced. However, this method is still far apart from original advantages of a metal denture, i.e., being thin and strong. Further, for a complete adaptation, a patient needs to see a dentist three to ten times to adjust the denture base by individually checking adaptation from the professional viewpoint of a dentist over a certain long period.

[0027]

Contrastingly, the denture base made of the amorphous alloy of the present invention can be reformed for adaptation very easily using, for example, a heating tool such as a soldering iron. More specifically, a soldering iron heated to approximately 300 degrees C is pressed against a portion which is, according to a complaint of a patient, in contact with the dry structure, and thereby this portion can be recessed easily. A hygienically undesirable portion having a clearance can be deformed into a protruding shape by being pressed by the soldering iron from its backside. Thus, in

any vent, the denture base of the present invention has a large advantag that it can be reformed through a very simple process as compared with the adaptation and reform process for the conventional denture base.

[0028]

It is necessary, in accordance with purposes, that the soldering iron used in this adaptation and reform process has its front end rounded suitably for pressing, and has a function of controlling a temperature. It is preferable that the soldering iron comprises an auxiliary means which, based on a product of temperature and time, rings a buzzer in a short time in case of high temperature and in a long time in case of low temperature. Further, in the present invention, a sandwiching-type tool such as tweezers or pliers can also be used for adjusting a spring pressure of the clasps and the retainers.

[0029]

Next, a denture base for a bridge denture will be described. When one or some teeth are lost, the bridge denture makes up for the lost portion by using the remaining teeth adjacent thereto as a support footing. In this case, when a denture base itself is manufactured by a casting method, a contraction occurs and dimensional accuracy disorders.

[0030]

Thus, in manufacturing a denture base for the bridge denture as well, the amorphous alloy of the present invention can be used, to provide the same advantages as those of the denture base for the previously-described denture. More specifically, although a specific illustration is omitted, cap-shaped crowns corresponding to adjacent two teeth to serve as a support footing are maintained within a temperature range from the glass transition temperature Tg to the crystallization temperature Tx and, in this condition, are molded by being pressed onto a working model by means of a heating iron. Then, a denture bridge corresponding to the lost teeth is connected between these crowns, and whole of it is given a form of a teeth profile. As a result, in this case as well, there can be obtained a denture base which is inexpensive, excellent in adaptability, and high in intensity. An implant-type attachment, etc., can be used in order to connect the crowns serving as the denture base and the denture bridge corresponding to the lost teeth to each other.

[0031]

[EFFECT OF THE INVENTION]

As described above, since the denture base of the present invention is made of the amorphous alloy having the supercooled liquid region, the denture base has excellent characteristics of doing no harm to living bodies and being chemically stable

even within a mouth. Moreover, a heating up to a predetermined temperature and a highly-accurate superplastic forming can be performed through a simpler process than the conventional titanium-pressing process. As a result, there can be obtained for the first time a metal denture base which is inexpensive, excellent in adaptability, and high in intensity. In addition, a process for reforming and adapting the denture base becomes pretty convenient as compared with the conventional ones, because the process can easily be performed by heating up to a predetermined temperature and applying only a relatively small force thereto.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1]

FIG. 1 is an explanatory view showing a method for manufacturing a bulk material serving as a specimen.

[FIG. 2]

FIG. 2 is an explanatory view showing results of diffractions by an X-ray diffractometer.

[FIG. 3]

FIG. 3 is an explanatory view showing results of differential scanning calorimetry.

[FIG. 4]

FIG. 4 is an explanatory view showing a constitutional ratio of three elements and a composition-dependency of a supercooled liquid region.

[FIG. 5]

FIG. 5 is an explanatory view showing stress-strain curves as plotted against variation in temperature.

[FIG. 6]

FIG. 6 is an explanatory view showing a method for manufacturing an amorphous alloy plate.

[FIG. 7]

FIG. 7 is an explanatory view showing an example of a working model.

[FIG. 8]

FIGS. 8(A) and 8(B) are explanatory views showing a step of forming a denture base from an amorphous alloy plate using a working model.

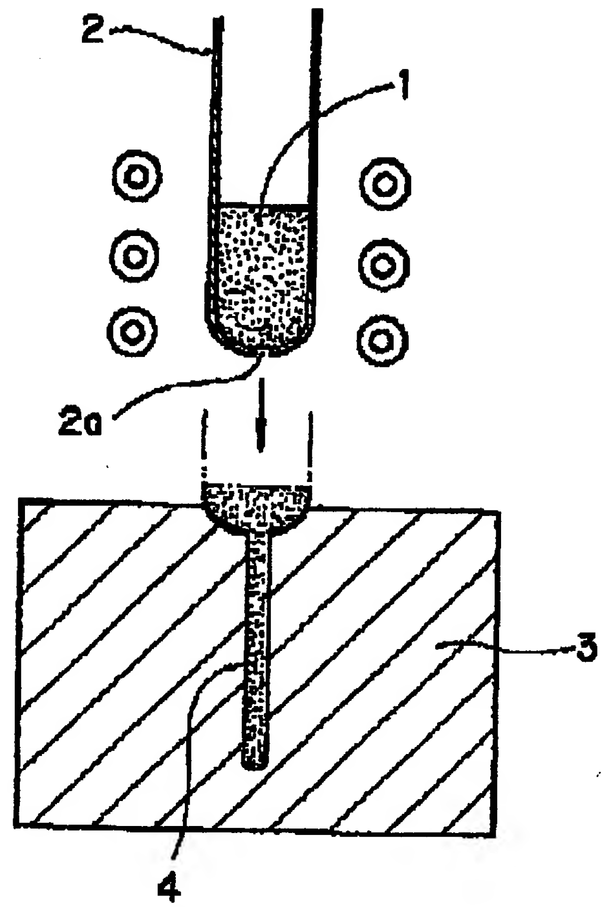
[EXPLANATION OF REFERENCE NUMERALS]

6 amorphous alloy plate

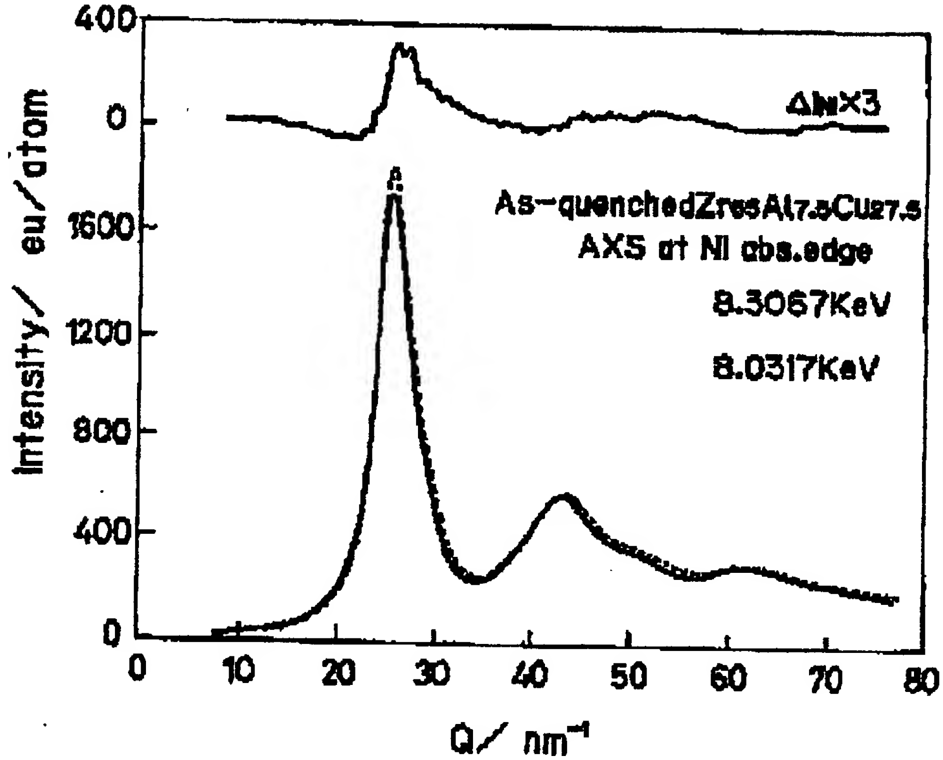
10 working model

21 heating furnace

[FIG. 1]



[FIG. 2]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0
1600
1200
800
400
0
Intensity / eu/atom
ΔNiX3
As-quenchedZr65Al7.5Cu27.5
AXS at Ni abs.edge
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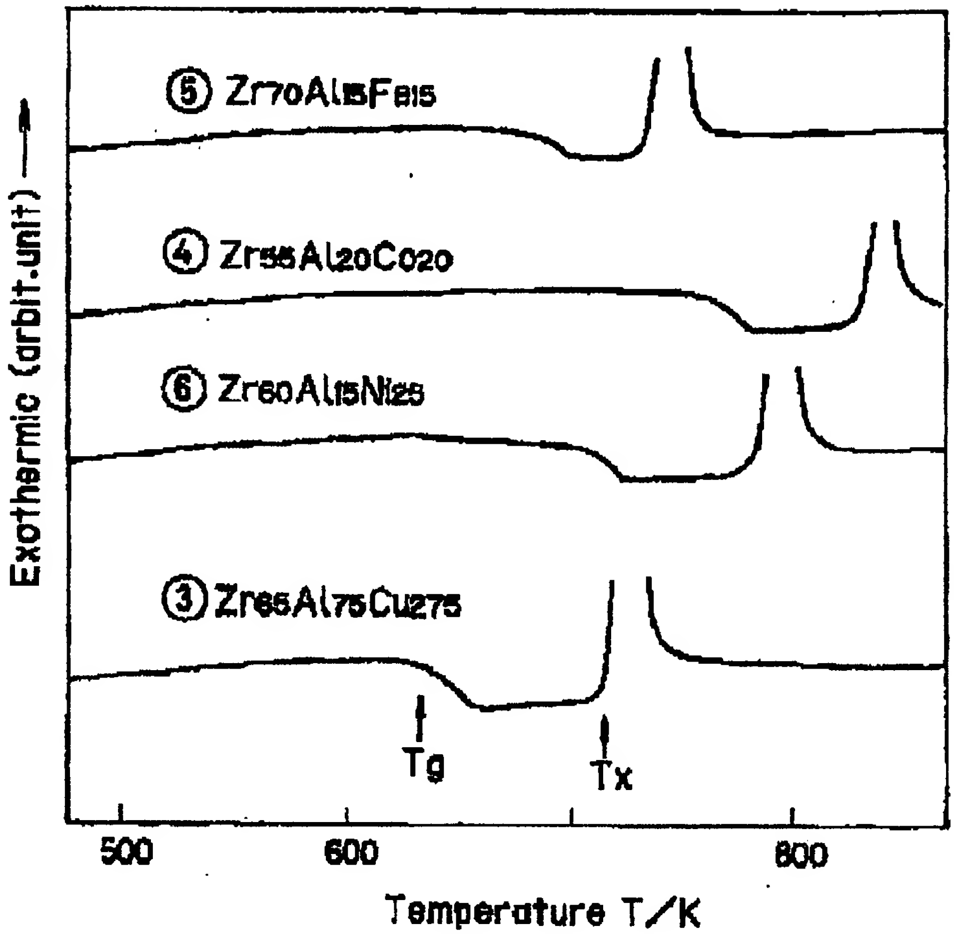
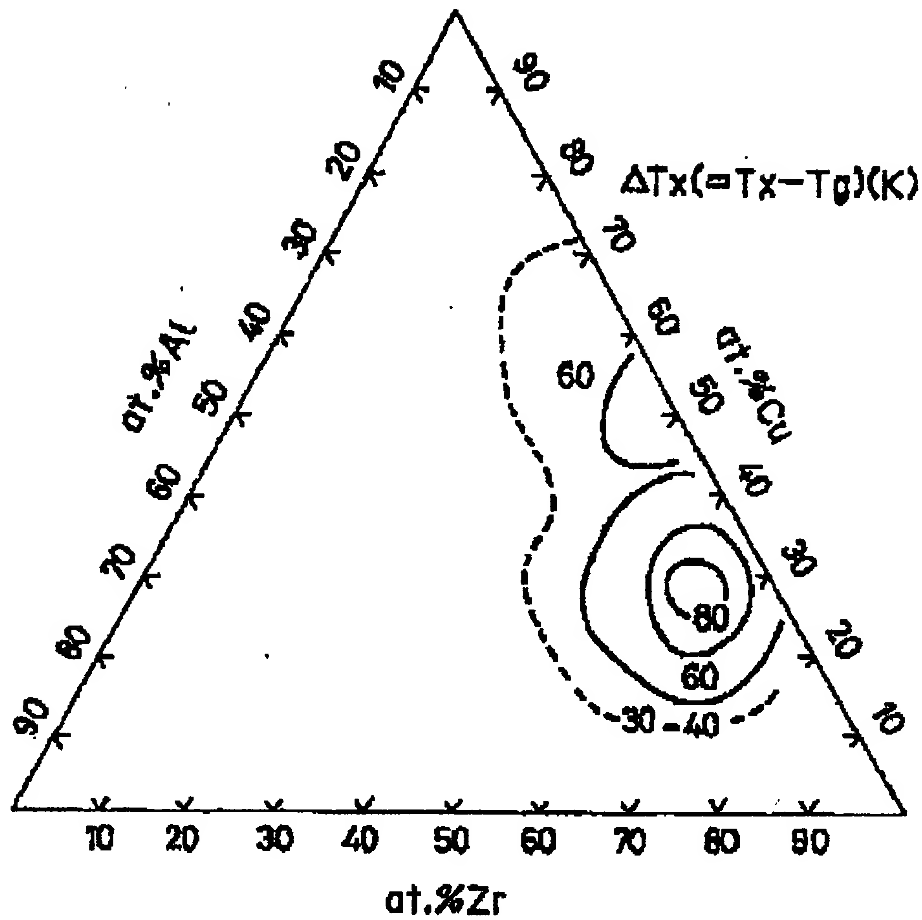
8.0317KeV
0
10
20
30
40
50
60
70
80
Q / nm⁻¹

[FIG. 3]

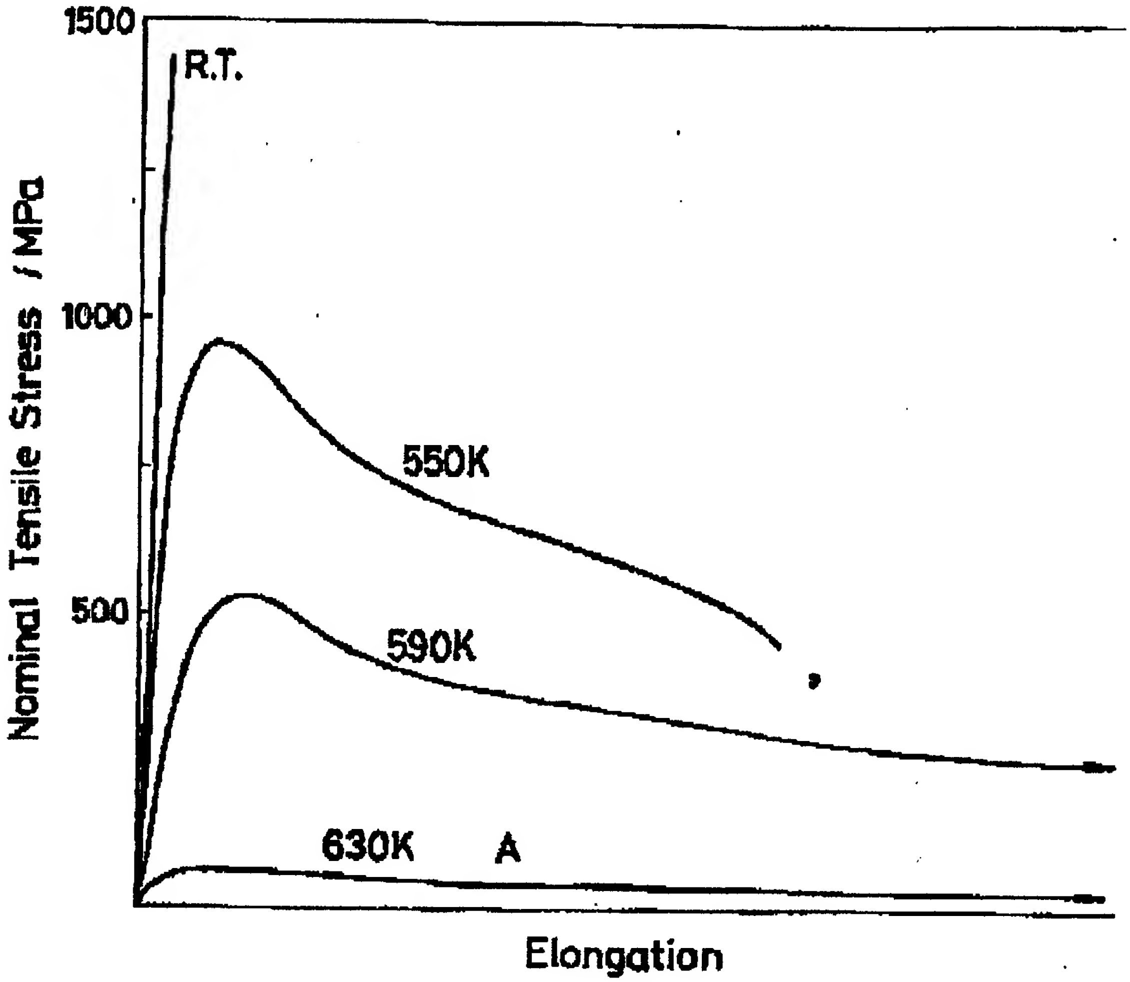


⑤ Zr70Al15Fe15
④ Zr55Al20Co20
⑥ Zr60Al15Ni25
③ Zr65Al7.5Cu27.5
Tg
Tx
500
600
800
Temperature T/K
Exothermic (arbit.unit)

[FIG. 4]



[FIG. 5]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1000
500
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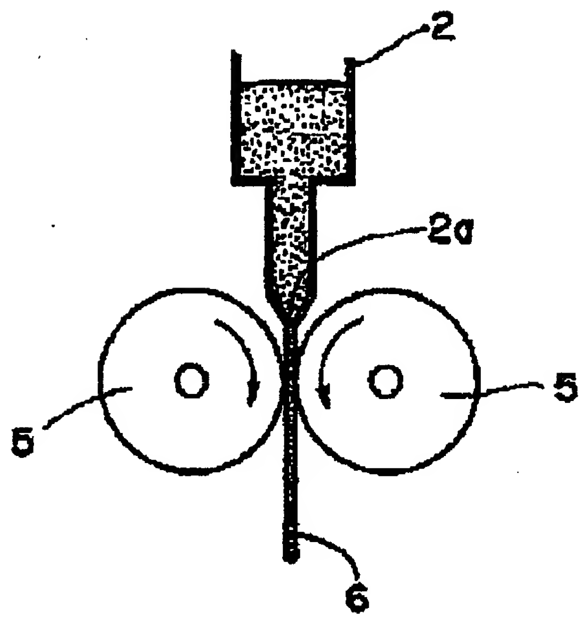
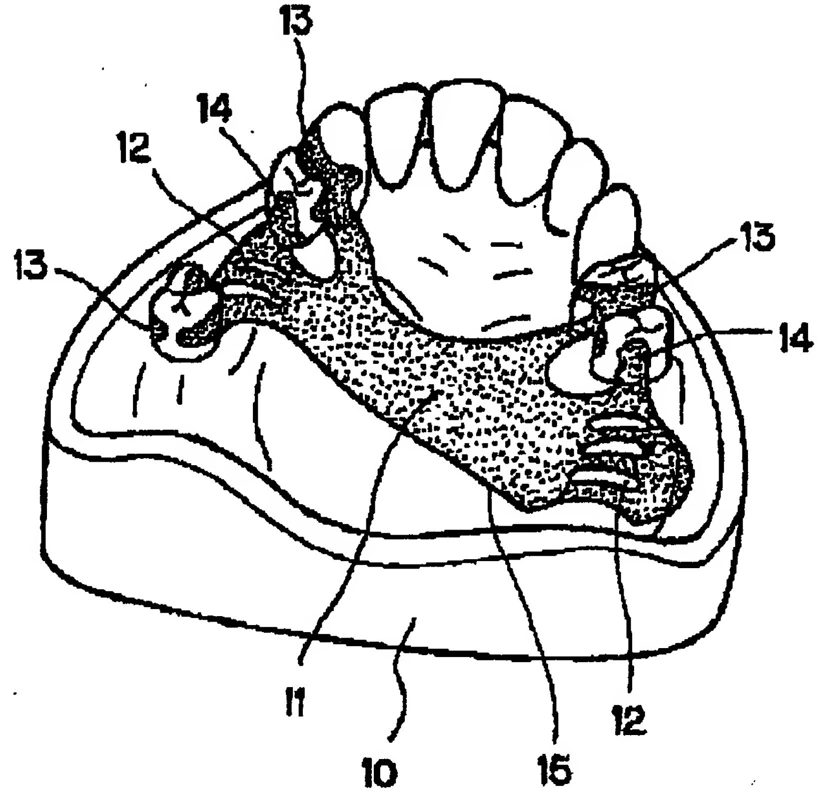
R.T.
550K
590K
630K
A
Elongation

[FIG. 6]

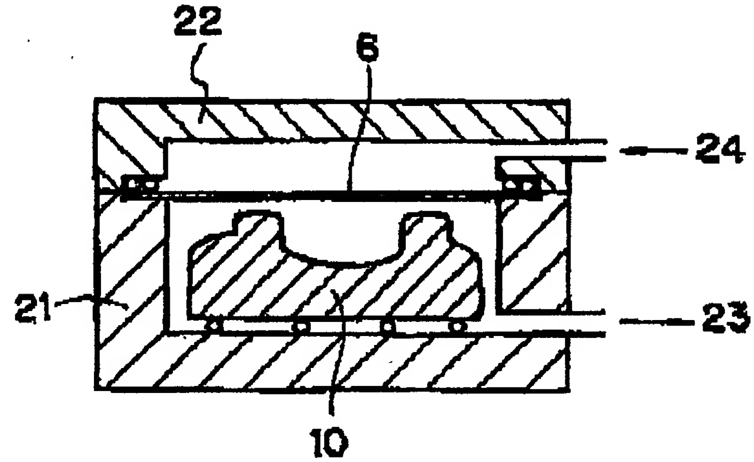


[FIG. 7]

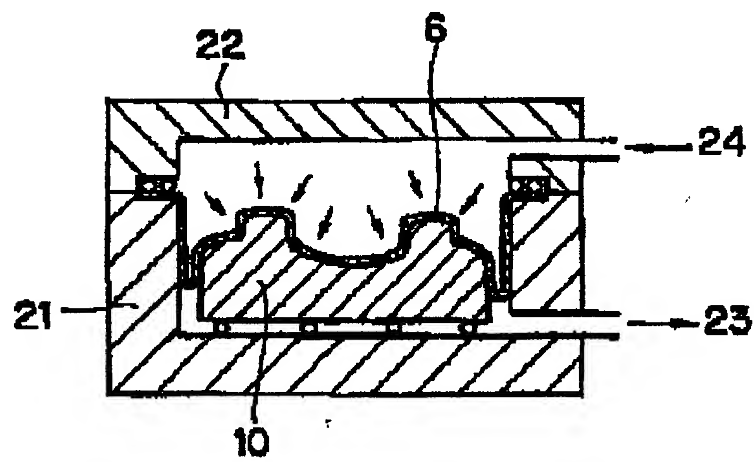


[FIG. 8]

(A)



(B)



VERIFICATION OF TRANSLATION

RE: US PATENT APPLICATION NO. 09/893,138

I, Megumi KAWASE, c/o KAJI, SUHARA & ASSOCIATES of Recruit Shin Osaka BLDG. 14-22, Nishinakajima 5-chome, Yodogawa-ku, Osaka-shi, Osaka 532-0011 JAPAN am the translator of Japanese Patent (Unexamined) Laid-Open No. 8-131461 and I state that the following is a true translation to the best of my knowledge and belief.

Signature of Translator Megumi Kawase

Megumi KAWASE

Dated May 10, 2004